

# PATENT SPECIFICATION

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NO DRAWINGS

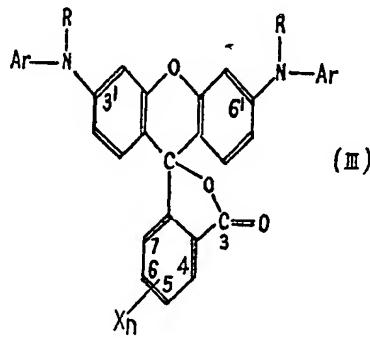
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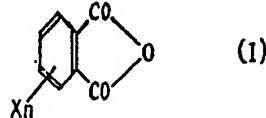


## (54) FLUORANE COMPOUNDS AND THEIR PREPARATION

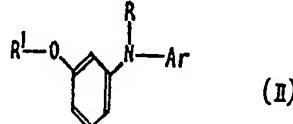
(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami Ashigara-Machi, Ashigara-Kamigun, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—  
 The present invention relates to a process for preparing colourless fluorane derivatives. According to the invention, there is provided a fluorane compound represented by the following general formula (III):



wherein each R is an alkyl group having from 1 to 5 carbon atoms, each Ar is an aryl group, X is a halogen atom, and n is an integer from 1 to 4.  
 Also according to the invention, there is provided a process for preparing a fluorane compound as claimed in Claim 1 which comprises condensing a phthalic anhydride derivative represented by the general formula (I):



wherein X represents a halogen atom and n is an integer from 1 to 4, with an N-alkyl-N-aryl-meta-aminophenol derivative represented by the general formula (II):



wherein R represents an alkyl group having from 1 to 5 carbon atoms, Ar represents an aryl group and R' represents a hydrogen atom, an acyl group, an arylsulphonyl group, an alkyl group having from 1 to 5 carbon atoms or an aralkyl group.

The invention also embraces copying papers which contain the aforesaid fluorane derivatives.

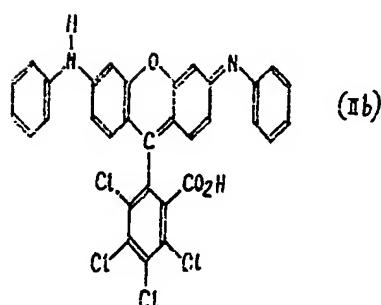
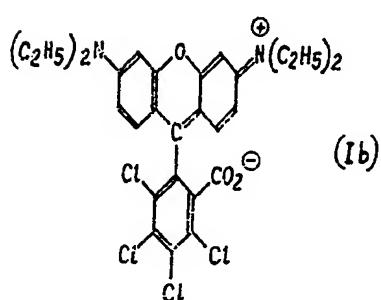
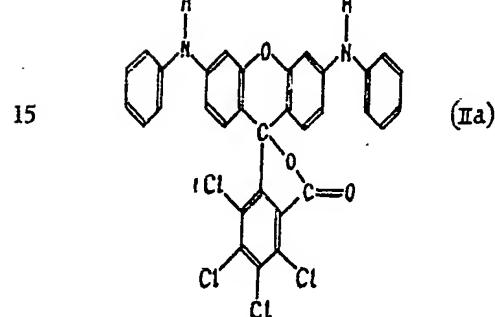
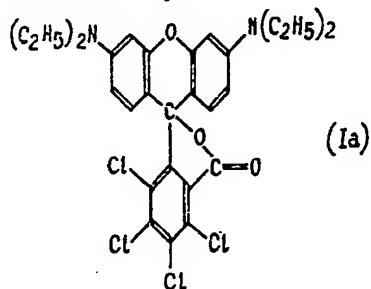
The fluorane compounds represented by the general formula (III) are substantially colourless in themselves but when in contact with solid acids such as bentonite, zeolite, acid clay and trimagnesium silicate, organic acid materials such as benzoic acid, benzenesulphonic acid and phenol, and mineral acids such as hydrochloric acid, sulphuric acid and perchloric acid, that is, the so-called electron acceptor materials, the fluorane compound immediately acquires a colour, varying from purple to blue depending on the particular compound.

The fluorane compounds represented by the general formula (III) are very stable on exposure to the atmosphere or to light and such exposure does not affect their colour-forming ability on contact with electron acceptors.

Also the colour dye formed on contact with said electron acceptor material is very fast to light. The fluorane compounds represented by the general formula (III) having the above-described properties are, therefore, very effective as precursors or colour-formers for pressure-sensitive, heat-sensitive and photo-sensi-

tive copying papers (these are developed by contact with the electron acceptor material under pressure, heat or light, respectively).

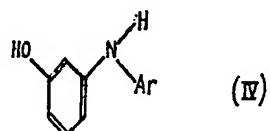
Heretofore, three have been known several compounds analogous to the compounds represented by the general formula (III); see "Beilstein, Handbuch Der Organische Chemie", vol. 19, page 349. These compounds may be represented, for example, by the following formulae Ia and IIa but are not obtained as colorless crystals. They are more accurately represented by the formulae Ib and IIb which are dyes.



The inventors have found that replacement of the dialkylamino or monoarylamino group at the 3'- and 6' positions on the fluorane with N - alkyl - N - arylamino groups renders the lactone ring stable, thereby yielding the desired compound as a colourless material.

A possible reason for the compound (Ia) not being obtained as a colourless compound is that the form represented by the formula (Ib) is more stable because the electron density at the nitrogen atom is high. Also, a reason for the compound (IIa) not being obtained as a colourless compound is that the quinoid structure of the formula (IIb) is more stable because of the presence of a very labile hydrogen atom.

The compounds represented by the general formula (I) for use in producing the fluorane compound represented by the general formula (III) may be selected from hitherto known compounds, such as 3,4,5,6 - tetrachlorophthalic anhydride, 3,4,5,6 - tetrabromophthalic anhydride, 3,4,6 - trichlorophthalic anhydride, 4,5 - dibromophthalic anhydride, 4 - bromo - 5 - chlorophthalic anhydride, 3 - chlorophthalic anhydride or 4 - iodophthalic anhydride. The compound of general formula (II) for reacting with the compound of the general formula (I) can be prepared by dehydration - condensation of resorcinol with an arylamine or can be synthesized from an N - aryl - meta - aminophenol represented by the general formula (IV);



That is to say, an N - alkyl - N - aryl - meta - aminophenol of the general formula (IV) wherein R' is a hydrogen atom can easily be obtained simply by directly N-alkylating the compound represented by the general formula (IV) with an alkylating agent such as a dialkyl sulphate, alkyl *p*-toluenesulphonate or an alkyl chloride in a solvent such as toluene, xylene or chlorobenzene, optionally in the presence of an alkaline catalyst and/or by the steps of acylating or arylsulphonylating the hydroxyl group in the compound of general formula (IV) with an acid anhydride or an acid chloride in the presence of an alkali, N-alkylating the acylated or the arylsulphonylated compound with an alkylating agent in the presence of a alkaline catalyst and saponifying the compound thus obtained (represented by the general formula (II) wherein R' is an acyl or an arylsulphonyl group) in good yield.

Further, the N - alkyl - N - aryl - meta -

aminophenyl ether of the general formula (II) wherein R is an alkyl group having from 1 to 5 carbon atoms can also be obtained by subjecting the compound represented by the general formula (IV) to O- and N-alkylation simultaneously with an alkylating agent in the presence of an alkali.

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The copying papers of the invention can be prepared in any known manner and may contain the fluorane in an oily solvent in micro-capsules coated onto a sheet support.

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The following Synthesis Examples will illustrate more specifically the syntheses of typical N - alkyl - N - aryl - meta - aminophenol derivatives represented by the general formula (II).

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**SYNTHESIS EXAMPLE 1**  
Synthesis of N-methyl-N-phenyl-meta-aminophenol

20 A solution of 74.0 g (0.4 mole) of N-phenyl-meta-aminophenol and 50.4 g (0.4 mole) of dimethyl sulphate in 150 ml of toluene was heated on a steam bath with stirring in a 500 ml three necked flask. When the temperature of the system reached about 80°C, the reaction was initiated violently and the temperature reached the boiling point of toluene. Thereafter, the heating was continued on the steam bath for 4 hours. The reaction mixture was then poured into a solution of 43 g (0.4 mole) of sodium carbonate in 400 ml of water and the toluene layer was separated from the aqueous layer. The toluene layer was washed twice with 150 ml of warm water, the toluene was distilled off under reduced pressure, and the residue was distilled in vacuo to obtain 54 g of N-methyl-N-phenyl-meta-aminophenol having a boiling point of 139—144°C/0.6 mm Hg.

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**SYNTHESIS EXAMPLE 2**  
Synthesis of N-ethyl-N-phenyl-meta-aminophenol

40 A solution of 93 g (0.5 mole) of N-phenyl-meta-aminophenol and 100 g (0.5 mole) of ethyl *p*-toluenesulphonate in 200 ml of xylene was reacted on an oil bath with stirring for 45 4 hours at the boiling point of xylene.

Thereafter, the reaction mixture was treated in the same manner as in Synthesis Example 1 to obtain 78 g of N - ethyl - N - phenyl - meta - aminophenol having a boiling point of 144—148°C/0.6 mm Hg.

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**SYNTHESIS EXAMPLE 3**  
Synthesis of N-isoamyl-N-phenyl-meta-aminophenol

55 A solution of 93 g (0.5 mole) of N-phenyl-meta-aminophenol and 76 g (0.5 mole) of isoamyl bromide in 100 ml of chlorobenzene was reacted for 4 hours in a sealed tube at 150—156°C. Thereafter, the reaction mixture was treated in the same manner as in Synthesis Example 1 to obtain 74 g of N-

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isoamyl - N - phenyl - meta - aminophenol having a boiling point of 154—158°C/0.4 mm Hg.

**SYNTHESIS EXAMPLE 4**  
Synthesis of other N-alkyl-N-aryl-meta-aminophenols

N - (*o* - tolyl) - meta - aminophenol and N - (*p* - anisyl) - meta - aminophenol were each methylated or ethylated in the same manner as in Synthesis Example 2. Also, N - (*o* - anisyl) - meta - aminophenol, N - (*p* - chlorophenyl) - meta - aminophenol, N - (*m* - chlorophenyl) - meta - aminophenol, N - diphenyl - meta - aminophenol and N - (*α* - naphthyl) - meta - aminophenol were methylated in the same manner as in Synthesis Example 1 to obtain the following N - alkyl - N - aryl - meta - aminophenols in yield of about 60%.

N - methyl - N - (*o* - tolyl) - meta - aminophenol: b.p. 140—144°C/0.5 mm Hg  
N - ethyl - N - (*p* - anisyl) - meta - aminophenol: b.p. 158—162°C/0.5 mm Hg  
N - methyl - N - (*o* - anisyl) - meta - aminophenol: b.p. 151—154°C/0.5 mm Hg  
N - methyl - N - (*p* - chlorophenyl) - meta - aminophenol: b.p. 143—146°C/0.3 mm Hg  
N - methyl - N - (*m* - chlorophenyl) - meta - aminophenol: b.p. 142—144°C/0.3 mm Hg  
N - methyl - N - diphenyl - meta - aminophenol: b.p. 168—172°C/0.2 mm Hg  
N - methyl - N - (*α* - naphthyl) - meta - aminophenol: b.p. 182—186°C/0.2 mm Hg.

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**SYNTHESIS EXAMPLE 5**  
Synthesis of 3-acetoxy- and 3-(*p*-toluenesulphonyloxy)-N-methyldiphenylamine

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3 - acetoxy- or 3 - (*p* - toluenesulphonyloxy) - diphenylamine, obtained by reacting 3 - hydroxydiphenylamine with one mole of acetic anhydride or *p* - toluenesulphonyl chloride in pyridine in the conventional manner, was methylated with dimethyl sulphate in the presence of anhydrous potassium carbonate in methanol to obtain 3 - acetoxy - N - methyldiphenylamine (b.p. 112—115°C/0.3 mm Hg) and 3 - (*p* - toluenesulphonyloxy) - N - methyldiphenylamine (b.p. 62—64°C) in a yield of 88—92%.

**SYNTHESIS EXAMPLE 6**  
Synthesis of 3-methoxy-4'-chloro-N-methyl-diphenylamine

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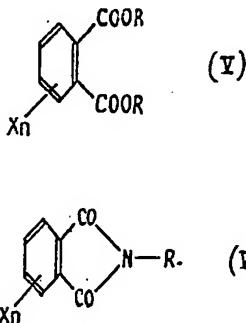
A mixture of 88 g (0.4 mole) of 3-hydroxy-4' - chlorodiphenylamine, 106 g (1 mole) of anhydrous sodium carbonate, 149 g (0.8 mole) of methyl *p* - toluenesulphonate and 300 ml of methanol was boiled on a steam bath for 5 hours.

The reaction mixture was poured into a

large quantity of water and then extracted with 500 ml of toluene. The toluene was distilled off under reduced pressure and the residue was then distilled in vacuo to obtain 5 62 g of 3 - methoxy - 4' - chloro - N - methylidiphenylamine (b.p. 138-142°C/0.3 mm Hg.).

The compound represented by the general formula (III) was also successfully produced 10 by heating a phthalic anhydride derivative of the formula (I) with an N - alkyl - N - aryl - meta - aminophenol derivative represented by the general formula (II) in the presence of a condensing agent such as sulphuric acid, *p* - toluenesulphonic acid, phosphoric acid, phosphoric anhydride, phosphosphoric acid or zinc chloride. The reaction may be conducted at 60-200°C, preferably 170-200°C for 1-6 hours. When the compound 15 represented by the following general formula V or VI was used instead of a phthalic anhydride derivative represented by the general formula (I), the fluorane compound represented by the general formula III could be 20 produced.

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(wherein X is a halogen atom; n is an integer from 1 to 4; and R is a hydrogen atom, an alkali metal atom, an alkyl group, an aryl group, an alkyl group, an acyl group or an arylsulphonyl group).

30 However, this reaction is believed to comprise the reaction between a phthalic anhydride derivative of the general formula (I), formed during the reaction, and the N-alkyl-N - aryl - meta - aminophenol represented by the general formula (II).

The present invention will be illustrated 35 by the following Examples.

40 EXAMPLE 1  
Production of 3',6' - bis(N - methyl - N - phenylamino) - 4,5,6,7 - tetrachlorofluorane  
A mixture of 20 g of N - methyl - N - phenyl - meta - aminophenol, 14.3 g of tetrachlorophthalic anhydride and 15 g of *p* - toluenesulphonic acid was reacted for 2 hours at 160-163°C, for 1.5 hours at 170-174°C and for 1.5 hours at 180-185°C while stirring the mixture on an oil bath. Thereafter,

50 the pigment salt formed in the reaction was dissolved in methanol, and the solution was poured into a large quantity of water. The precipitated pigment salt was filtered off, and then stirred vigorously in a suspension of 300 ml of 3% by weight aqueous sodium hydroxide solution and 300 ml of toluene to dissolve the salt in the toluene after being neutralized.

55 The toluene layer was separated, washed several times with warmed water and thereafter the toluene was distilled off under reduced pressure. The syrup-like material thus obtained was mixed with a small quantity of acetone and cooled to obtain 16.8 g of 3',6' - bis(N - methyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane as a faint greyish - blue crystal having a melting point of 240-241°C.

60 A toluene solution of said fluorane compound was completely colourless but the solution turned a slightly purplish blue colour as soon as it was contacted with such electron acceptor materials as acid clay, benzenesulphonic acid and hydrochloric acid.

65 EXAMPLE 2  
Production of 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane

70 A mixture of 21.3 g of N - ethyl - N - phenyl - meta - aminophenol, 14.3 g of tetrachlorophthalic anhydride and 20 g of zinc chloride was reacted for 5 hours at 180-190°C. The reaction mixture was treated in the same manner as in Example 1 to obtain 12.3 g of 3',6' - bis(N - ethyl - N - phenyl - amino) - 4,5,6,7 - tetrachloro - fluorane as a faint greyish-blue crystal having a melting point of 225°C. Said fluorane compound turned a slightly purplish blue colour on being contacted with electron acceptors as in Example 1.

75 EXAMPLE 3  
Production of 3',6' - bis[N - methyl - N - (o - tolyl)amino] - 4,5,6,7 - tetrachloro - fluorane

80 A mixture of 21.3 g of N - methyl - N - (o - tolyl) - meta - aminophenol, 14.3 g tetrachlorophthalic anhydride, 15 g of *p* - toluenesulphonic acid and 5 g of zinc chloride was reacted for 5 hours at 170-180°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 15.8 g of 3',6' - bis[N - methyl - N - (o - tolyl)amino] - 4,5,6,7 - tetrachloro - fluorane as a faintly purplish crystal having a melting point of 259-261°C.

85 Said fluorane compound developed a purple colour when contacted with electron acceptors as in Example 1.

90 EXAMPLE 4  
Production of 3',6' - bis[N - methyl - N - (o - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane

95 A mixture of 22.9 g of N - methyl - N -

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5 (o - anisyl) - meta - aminophenol, 14.3 g of tetrachlorophthalic anhydride, 15 g of *p*-toluenesulphonic acid and 5 g of phosphoric anhydride was reacted for 4 hours at 165—175°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 18.2 g of 3',6' - bis[N - methyl - N - (o - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane as a faint purple crystal having a melting point of 213°C. Said fluorane compound developed a purplish blue colour on being contacted with electron acceptor materials as in Example 1.

10 EXAMPLE 5  
15 Production of 3',6' - bis[N - methyl - N - (p - chlorophenyl)amino] - 4,5,6,7 - tetrachlorofluorane  
A mixture of 23.4 g of N - methyl - N - (p - chlorophenyl) - meta - aminophenol, 14.3 g of tetrachlorophthalic anhydride, 10 g of zinc chloride, 10 g of 85% phosphoric acid and 5 g of phosphoric anhydride was reacted for 3 hours at 185—195°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 13.3 g of 3',6' - bis[N - methyl - N - (p - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane as a colourless crystal having a melting point of 223°C.

20 25 30 Said fluorane compound developed a blue colour on being contacted with an electron acceptor material as in Example 1.

EXAMPLE 6  
35 Production of 3',6' - bis[N - ethyl - N - (p - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane  
A mixture of 24.3 g of N - ethyl - N - (p - anisyl) - meta - aminophenol, 14.3 g of tetrachlorophthalic anhydride and 30 g of polyphosphoric acid was reacted for 2 hours at 120—125°C, for 1.5 hour at 140—145°C and for 1 hour at 160—165°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 15.3 g of 3',6' - bis N - ethyl - N - (p - anisyl)amino - 4,5,6,7 - tetrachloro - fluorane as a faint greyish-blue crystal having a melting point of 231—232°C.

40 45 Said fluorane compound developed a blue colour on being contacted with an electron acceptor material as in Example 1.

50 EXAMPLE 7  
55 Production of 3',6' - bis N - methyl - N - (m - chlorophenyl)amino - 4,5,6,7 - tetrachloro - fluorane  
A mixture of 23.4 g of N - methyl - N - (m - chlorophenyl) - meta - aminophenol, 14.3 g of tetrachlorophthalic anhydride, 20 g of 80% sulphuric acid and 20 g of polyphosphoric acid was reacted for 3 hours at 120—130°C and for 1 hour at 140—145°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 8.7 g of 3',6' - bis N - methyl - N - (m - chlorophenyl)amino - 4,5,6,7 - tetrachloro - fluorane as a colourless crystal having a melting point of 160—162°C. Said fluorane compound developed a purplish-blue colour on being contacted with an electron acceptor material as in Example 1.

60 EXAMPLE 8  
70 Production of 3',6' - bis[N - methyl - N - (p - chlorophenyl)amino] - 4,5,6,7 - tetrabromo - fluorane  
A mixture of 23.2 g of N - methyl - N - (p - chlorophenyl) - meta - aminophenol, 23.2 g of tetrabromophthalic anhydride, 30 g of *p*-toluenesulphonic acid and 5 g of phosphoric anhydride was reacted for 4 hours at 170—175°C.

75 80 Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 21.6 g of 3',6' - bis N - methyl - N - (p - chlorophenyl)amino - 4,5,6,7 - tetrabromo - fluorane as a colourless crystal melting at 248—250°C. Said fluorane compound developed a blue colour on being contacted with an electron acceptor material as in Example 1.

85 EXAMPLE 9  
90 Production of 3',6' - bis[N - methyl - N - (p - chlorophenyl)amino] - 4,7 - dichloro - fluorane  
A mixture of 23.4 g of N - methyl - N - (p - chlorophenyl) - meta - aminophenol, 108 g of 3,6 - dichlorophthalic anhydride, 15 g of *p*-toluenesulphonic acid, 19 g of zinc chloride and 3 g of phosphoric anhydride was reacted for 2 hours at 175—180°C and for 2 hours at 190—195°C.

95 100 Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 18.4 g of 3',6' - bis N - methyl - N - (p - chlorophenyl)amino - 4,7 - dichloro - fluorane as a colourless crystal melting at 200—202°C.

105 Said fluorane compound developed a slightly purplish blue colour on being contacted with an electron acceptor material as in Example 1.

110 EXAMPLE 10  
115 Production of 3',6' - bis(N - isoamyl - N - phenylamino) - 5(or 6) - iodo - fluorane  
A mixture of 25.5 g of N - isoamyl - N - phenyl - meta - aminophenol, 13.7 g of 4 - iodophthalic anhydride, 15 g of *p*-toluenesulphonic acid and 15 g of polyphosphoric acid was reacted for 5 hours at 160—170°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 12.5 g of a mixture of 3',6' - bis(N - isoamyl - N - phenylamino) - 5 - iodo - fluorane and 3',6' - bis(N - isoamyl - N - phenylamino) - 6 - iodo - fluorane as a faint purple crystalline material melting at 88—

102°C. This fluorane compound developed a purple colour on being contacted with an electron acceptor material as in Example 1.

**EXAMPLE 11**

5 Production of 3',6' - bis N - methyl - N - (p - chlorophenyl)amino - 5(or 6) - bromo - 6(or 5)-chloro-fluorane

A mixture of 23.4 g of N - methyl - N - (p - chlorophenyl) - meta - aminophenol, 13.1 g of 4 - bromo - 5 - chlorophthalic anhydride, 15 g of zinc chloride and 15 g of polyphosphoric acid was reacted at 160 - 170°C for 5 hours.

15 Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 13.8 g of a mixture of 3',6' - bis[N - methyl - N - (p - chlorophenyl)amino] - 5 - bromo - 6 - chloro - fluorane and 3',6' - [N - methyl - N - (p - chlorophenyl)amino] - 6 - bromo - 5 - chloro - fluorane as a colourless crystalline material melting at 143 - 152°C.

20 This fluorane compound mixture developed a purple colour on being contacted with an electron acceptor material as in Example 1.

25 **EXAMPLE 12**

Production of 3',6' - bis(N - methyl - N - diphenylamino) - 5(or 6) - bromo - 6(or 5) - chloro-fluorane

30 A mixture of 27.5 g of N - methyl - N - diphenyl - meta - aminophenol, 13.1 g of 3 - chloro - 4 - bromophthalic anhydride, 20 g of p - toluenesulphonic acid and 5 g of phosphoric anhydride was reacted for 3 hours at 175 - 180°C, and for 2 hours at 190 - 200°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 15.6 g of a mixture of 3',6' - bis - (N - methyl - N - diphenylamino) - 5 - bromo - 6 - chloro - fluorane with 3',6' - bis(N - methyl - N - diphenylamino) - 6 - bromo - 5 - chloro - fluorane as a colourless crystalline material melting at 178 - 188°C.

45 This fluorane compound mixture developed a bluish purple colour on being contacted with an electron acceptor material as in Example 1.

**EXAMPLE 13**

50 Production of 3',6' - bis[N - methyl - N - (α - naphthyl)amino] - 5(or 6) - bromo - 6(or 5)-chloro-fluorane

Example 12 was repeated except that 32.6 g of N - methyl - N - (α - naphthyl) - meta - aminophenol was used instead of 27.5 g of N - methyl - N - diphenyl - meta - aminophenol to obtain 18.8 g of a mixture of 3',6' - bis N - methyl - N - (α - naphthyl)amino - 5 - bromo - 6 - chloro - fluorane and 3',6' - bis N - methyl - N - (α - naphthyl)amino - 6 - bromo - 5 - chloro - fluorane as a colourless crystalline material melting at 204 - 212°C. This fluorane

65 compound mixture developed a purplish blue colour on being contacted with an electron acceptor material as in Example 1.

**EXAMPLE 14**

Another process for producing the compound synthesized in Example 1.

70 Example 1 was repeated except that 15.2 g of tetrachlorophthalic acid, 16.6 g of dimethyl tetrachlorophthalate, 14.3 g of tetrachlorophthalimide or 16.2 g of potassium tetrachlorophthalimide were used instead of 14.3 g of tetrachlorophthalic anhydride to obtain 3',6' - bis(N - methyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane, in each case in nearly the same yield (48 - 54%).

75 Consequently, it is believed that tetrachlorophthalic anhydride, formed during the reaction, is subjected to a condensation reaction with N - methyl - N - phenyl - meta-aminophenol.

80 The above mentioned tetrachlorophthalic acid derivatives used instead of tetrachlorophthalic anhydride are generally produced commercially from tetrachlorophthalic anhydride, and so are economically disadvantageous.

**EXAMPLE 15**

90 Another process for producing the compound synthesized in Example 1.

95 Example 1 was repeated except that 23.1 g of 3 - acetoxy - N - methyl diphenylamine or 35.3 g of 3 - (paratoluene-sulphonyloxy) - N - methyl diphenylamine was used instead of 20 g of N - methyl - N - phenyl - meta - aminophenol to obtain 3',6' - bis(N - methyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane. Nearly the same yield (52 - 55%) was obtained in each case.

100 Since the syntheses of 3 - acetoxy - N - methyl diphenylamine and 3 - (p - toluene-sulphonyloxy) - N - methyl diphenylamine are easier than that of N - methyl - N - phenyl - meta - aminophenol, the process of this Example is advantageous.

**EXAMPLE 16**

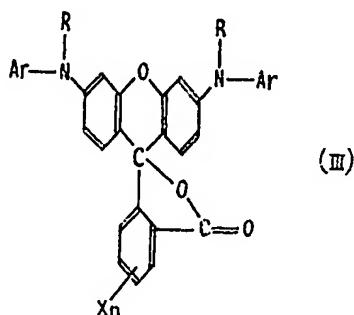
110 Another process for producing the compound synthesized in Example 5.

115 Example 5 was repeated except that 24.8 g of 3 - methoxy - 4' - chloro - N - methyl diphenylamine was used instead of 23.4 g of N - methyl - N - (p - chlorophenyl) - meta - aminophenol to obtain 9.8 g of 3',6' - bis[N - methyl - N - (p - chlorophenyl) amino] - 4,5,6,7-tetrachloro - fluorane.

120 The yield was somewhat inferior as compared with Example 5, but synthesis of 3 - methoxy - 4' - chloro - N - methyl diphenylamine is easier than that of N - methyl - N - (para-chlorophenyl) meta-aminophenol.

## WHAT WE CLAIM IS:—

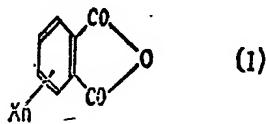
1. A fluorane compound represented by the following general formula (III):



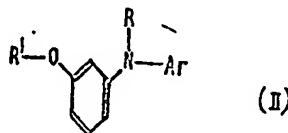
5 wherein each R is an alkyl group having from 1 to 5 carbon atoms, each Ar is an aryl group, X is a halogen atom, and n is an integer from 1 to 4.

10 2. A compound as claimed in Claim 1, substantially as hereinbefore described with reference to any of the Examples Nos. 1 to 16.

15 3. process for preparing a fluorane compound as claimed in Claim 1, which comprises condensing a phthalic anhydride derivative represented by the general formula (I):



20 wherein X represents a halogen atom and n is an integer from 1 to 4, with an N - alkyl - N - aryl - meta - aminophenol derivative represented by the general formula (II):



wherein R represents an alkyl group having from 1 to 5 carbon atoms, Ar represents an aryl group and R' represents a hydrogen atom, an acyl group, an arylsulphonyl group, an alkyl group having from 1 to 5 carbon atoms or an aralkyl group.

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4. A process as claimed in Claim 3, wherein said reaction is conducted in the presence of a condensing agent.

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5. A process as claimed in Claim 4, wherein condensing agent is sulphuric acid, *p*-toluene-sulphonic acid, phosphoric acid, phosphoric anhydride, polyphosphoric acid or zinc chloride.

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6. A process as claimed in Claim 3, 4 or 5, wherein said reaction is conducted at a temperature from 60 to 200°C for from 1 to 6 hours.

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7. A process for preparing a fluorane compound as claimed in Claim 1, substantially as hereinbefore described with reference to any of the Examples Nos. 1 to 16.

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8. A copying paper, which contains a compound as claimed in Claim 1 or 2.

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9. A process of colour-forming, which comprises contacting a fluorane compound as claimed in Claim 1 or 2 with an electron acceptor material.

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